

## Mechanism of Carbon Dioxide and Water; Incorporation in Ba<sub>2</sub>TiO<sub>4</sub>:

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## Article

## Mechanism of Carbon Dioxide and Water Incorporation in BaTiO<sub>3</sub>: A Materials Degradation Study

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# Mechanism of Carbon Dioxide and Water Incorporation in Ba<sub>2</sub>TiO<sub>4</sub>: a Joint Computational and Experimental Study.

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## Abstract

CO<sub>2</sub> incorporation in solids is attracting considerable interest in a range of energy-related areas. Materials degradation through CO<sub>2</sub> incorporation is also a critical problem with some fuel cell materials, particularly for proton conducting ceramic fuel cells. Despite this importance, the fundamental understanding of the mechanism of CO<sub>2</sub> incorporation is lacking. Furthermore, the growing use of lower temperature sol gel routes for the design and synthesis of new functional materials may be unwittingly introducing significant residual carbonate and hydroxyl ions into the material, and so studies such as the one reported here investigating the incorporation of carbonate and hydroxyl ions are important, to help explain how this may affect the structure and properties. This study on Ba<sub>2</sub>TiO<sub>4</sub> suggests highly unfavourable intrinsic defect formation energies, but comparatively low H<sub>2</sub>O and CO<sub>2</sub> incorporation energies in accord with experimental findings. Carbonate defects are likely to form in both pristine and undoped Ba<sub>2</sub>TiO<sub>4</sub> systems, whereas those based on H<sub>2</sub>O will only form in systems containing other supporting defects, such as oxygen interstitials or vacancies. However, both hydroxyl and carbonate defects will trap oxide ion defects induced through doping, and the results from both experimental and modelling studies suggest that it is primarily the presence of carbonate that is responsible for stabilising the high temperature  $\alpha'$ -phase at lower temperatures.

## 1 Introduction

The A<sub>2</sub>BO<sub>4</sub> material class is a diverse group of oxometallates with over 50 known crystal structures, many of which contain isolated or linked tetrahedral frameworks.<sup>1,2</sup> They are of huge technological importance and one such material is barium orthotitanate, relatively close to its electroceramic cousin BaTiO<sub>3</sub>. Numerous compounds exist within the BaO-TiO<sub>2</sub> system, several being good electroceramics.<sup>3,4</sup> Of these compounds, only barium orthotitanate (Ba<sub>2</sub>TiO<sub>4</sub>) is both barium-rich and stable.<sup>5,6</sup> This material has a high melting point of 1860 °C and is unusual as it has Ti<sup>4+</sup> ions tetrahedrally coordinated to oxygen.<sup>7,8</sup> It has recently gained a renewed interest due to its CO<sub>2</sub> sorption properties, which emanates from a reversible Ba<sub>2</sub>TiO<sub>4</sub> + CO<sub>2</sub> →

BaCO<sub>3</sub> + BaTiO<sub>3</sub> process, which makes it a promising candidate for carbon capture applications.<sup>9–13</sup> Like many other barium titanates, it is predicted to be a wide-gap insulator.<sup>14</sup>

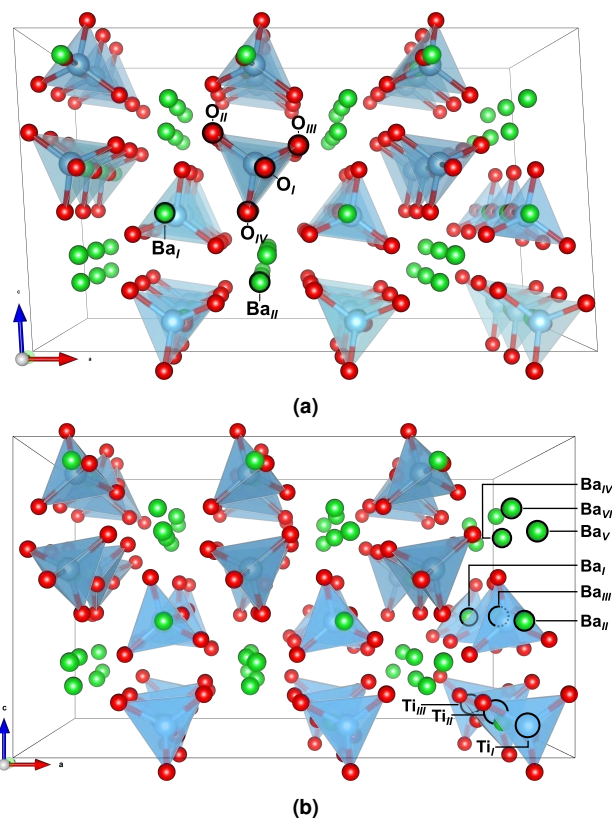
Ba<sub>2</sub>TiO<sub>4</sub> is highly hygroscopic and has been reported to exist in a low temperature monoclinic  $P2_1/n$   $\beta$ -phase and a high temperature orthorhombic  $P2_1nb$   $\alpha'$ -phase, the latter being a tripled  $b$ -axis superstructure of the former.<sup>15,16</sup> These studies have shown that the Ba<sub>2</sub>TiO<sub>4</sub> structure can be described as a series of isolated TiO<sub>4</sub> tetrahedra separated by Ba ions which occupy 7 (or 6 in the  $\alpha'$ -phase) and 8 coordinate sites, shown in Figure 1. Further studies have suggested that the phase transformation temperature can be affected by grain size and impurity effects, with some reports showing that lower temperature synthesis routes can stabilise the high temperature orthorhombic  $\alpha'$ -phase.<sup>17–20</sup> However, our prior work on Ba containing perovskite systems have shown that at such lower temperatures carbonate can be present in the structure.<sup>21</sup> In this paper, we therefore present a detailed modelling and experimental investigations, elucidating the mechanisms of CO<sub>2</sub> and H<sub>2</sub>O incorporation, and propose that it is CO<sub>2</sub> incorporation as carbonate, which is responsible for the stabilisation this phase.

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**Fig. 1** Structure of a)  $\beta$ -Ba<sub>2</sub>TiO<sub>4</sub> ( $3 \times 3 \times 1$  supercell) and b)  $\alpha'$ -Ba<sub>2</sub>TiO<sub>4</sub> ( $3 \times 1 \times 1$  supercell) with Ba, Ti and O ions represented as green, blue and red spheres respectively and TiO<sub>4</sub> tetrahedra in blue.

## 2 Methodology

### 2.1 Computational

The computational methods employed herein are reviewed in brief below, however more comprehensive descriptions can be found elsewhere.<sup>22–24</sup> Interatomic potential based energy minimisation calculations were performed using the general utility lattice program (GULP),<sup>25,26</sup> and structural images rendered using VESTA.<sup>27</sup>

Calculations were based on the Born model for ionic solids where long and short-range pairwise terms are used to describe the Coulombic, and the Pauli's repulsive and van der Waals interactions respectively. In this study, short-range ionic interactions were modelled using the Buckingham potential:<sup>28</sup>

$$\Phi_{ij}(r) = A_{ij} \exp\left(-\frac{r}{\rho_{ij}}\right) - \frac{C_{ij}}{r^6} \quad (1)$$

Where  $\Phi_{ij}$  is the potential energy resulting from the interaction of ions  $i$  and  $j$  at distance  $r$ , and  $A_{ij}$ ,  $\rho_{ij}$  and  $C_{ij}$  are the empirically derived potential parameters specific to the  $i-j$  ion pair. Ionic polarisability, which is particularly important when considering charged defects, was described using the Dick and Overhauser shell model.<sup>29</sup> Interatomic potentials, and shell parameters, from literature were screened to identify a preliminary model.<sup>30–32</sup> Each potential was then fitted to the experimental  $\beta$ -Ba<sub>2</sub>TiO<sub>4</sub> structure, and vetted to its respective binary oxide struc-

ture and elastic constants, to yield those in table 1.<sup>15</sup>

Intramolecular O-H and C-O interactions within the OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> units were modelled with the Coulomb-subtracted Morse potential, equation 2, as it better describes their covalent character.<sup>33</sup>

$$\Phi_{ij}(r) = D_e[(1 - \exp(-a(r - r_0)))^2 - 1] \quad (2)$$

Where  $D_e$  and  $a$  are depth and width of the potential well respectively and  $r_0$  is the equilibrium bond distance. The parameters selected to model OH<sup>-</sup> units in Ba<sub>2</sub>TiO<sub>4</sub> are given in table ??.<sup>34</sup> In accordance with Panchmatia *et al.*<sup>34</sup>, partial charges of -1.4263 and 0.4263 were placed on O and H respectively to model the OH<sup>-</sup> unit's dipole moment. The CO<sub>3</sub><sup>2-</sup> was treated with an O shell (-1.380) and a partial charge on the carbon (1.450). A three-body potential was also included to maintain the CO<sub>3</sub><sup>2-</sup> group's 120° bond angle. This, shown in equation 3, is parameterised by its equilibrium bond angle,  $\theta_0$ , and a constant,  $k_2$ .

$$\Phi_{ijk}(\theta_{ijk}) = \frac{1}{2}k_2(\theta_{ijk} - \theta_0)^2 \quad (3)$$

Finally, the torsional term shown in equation 4 is necessary to model the potential energy associated with the out-of-plane bending of the CO<sub>3</sub><sup>2-</sup> group. In the torsional potential,  $k_4$ ,  $\theta_0$  and  $n$  represent a constant, equilibrium torsion angle and number of stable minima respectively.

$$\Phi_{ijkl}(\theta_{ijkl}) = k_4(1 - \cos(n\theta_{ijkl} - \theta_0)) \quad (4)$$

The CO<sub>3</sub><sup>2-</sup> potential model used, table ??, is based on that by Archer *et al.*<sup>35</sup>, where all intramolecular interactions act on the oxygen's core, and includes Kerisit and Parker's<sup>36</sup> C-O<sub>Lattice</sub> Buckingham potential. The torsional  $k$  term was refined (1.10 eV) using *ab initio* quantum mechanical coupled cluster CCSD(T) methods in order to improve the model's stability.

Point defects were modelled using the Mott Littleton method.<sup>37</sup> This method partitions the area encompassing the defect into two spherical regions. Ions in the inner region are treated explicitly, while those in the outer region are handled more approximately by quasi-continuum methods.<sup>37</sup> Convergence tests for both regions showed no significant change to defect energy beyond a short-range Mott Littleton cut-off of 12.00 Å (inner region) and 24.00 Å (outer region) for single defect calculations and of 14.00 Å and 28.00 Å respectively for the molecular defect calculations. The CO<sub>3</sub><sup>2-</sup> defects were modelled using the supercell method.<sup>37</sup>

Defect reaction mechanisms are described herein using Kröger-Vink notation.<sup>38</sup> In this, a species is represented as  $A_x^q$ , where  $A$  corresponds to the ion itself or V if a vacancy. The subscript  $x$  represents the species' lattice site, and an  $i$  is used for interstitials. The superscript  $q$  is the species' effective electronic charge relative to the lattice site it occupies, with positive and negative charges represented by dots and primes respectively and no charge by a cross.

The deliberate choice of using a classical interatomic based approach was for many reasons listed below:

1) Given the number of calculations required and the size of each system, a DFT based approach would have been rather costly from a computational stand point.

Table 1 Interatomic potential and shell model parameters for Ba<sub>2</sub>TiO<sub>4</sub> used in this work

a) Buckingham potential parameters <sup>‡</sup> .			
Interaction	A (eV)	ρ (Å)	C (eV Å <sup>6</sup> )
Ba <sup>2+</sup> - O <sup>2-</sup>	4939.2	0.3074	0.00
Ti <sup>4+</sup> - O <sup>2-</sup>	1946.9	0.3020	9.22
O <sup>2-</sup> - O <sup>2-</sup>	22764.3	0.1490	28.33
b) Shell model parameters			
Ion	Shell Charge (e)	k (eV Å <sup>-2</sup> )	
O <sup>2-</sup>	-2.91	49.53	

‡ A short range potential cut-off of 12.00 Å was enforced in all static-lattice calculations.

2) All other aspects of the Ba<sub>2</sub>TiO<sub>4</sub> material investigation (for example defect formation, doping, defect clustering, proton defect formations) would also need to be conducted using DFT based methods to be consistent. This is particularly important when considering interactions between dopant incorporation and carbonate formation as classically calculated energy values would be added to DFT calculated ones introducing internal consistency issues.

3) A rigorously tested and verified classical interatomic based "Ba<sub>2</sub>TiO<sub>4</sub> - CO<sub>3</sub>" model, is the springboard for future molecular dynamics simulations, where investigations of the diffusion of absorbed carbonate and protonic defects in Ba<sub>2</sub>TiO<sub>4</sub> can be performed in larger simulation cells and for nanosecond simulation times. Besides, such methods have been successfully employed to provide atomistic level insights into carbonate and protonic defects in olivine, apatite-type and many other materials.<sup>39–43</sup>

2.2 Experimental

In order to compare with the modelling studies a 5 g sample of monoclinic Ba<sub>2</sub>TiO<sub>4</sub> was prepared by concomitantly mixing BaCO<sub>3</sub> and TiO<sub>2</sub> in the 2:1 molar ratio, and heating at 950 °C for 12 hours, before regrinding and reheating at 1100 °C for 12 hours and furnace cooling. The sample was analysed by X-ray powder diffraction (Bruker D8 diffractometer, Cu K<sub>α</sub> radiation), which confirmed the formation of the monoclinic β-Ba<sub>2</sub>TiO<sub>4</sub> phase. Approximately 0.5 g portions of this phase were heated under different conditions to investigate any transformation to the α'-Ba<sub>2</sub>TiO<sub>4</sub> phase. Subsequent analysis was performed using TG-MS (Netzsch STA 449 F1 Jupiter Thermal Analyser) to determine any mass losses. Samples were heated under N<sub>2</sub> with a heating rate of 10 °C min<sup>-1</sup> up to 1100 °C.

3 Results and Discussion

3.1 Structural Modelling and Intrinsic Defects

At room temperature, Ba<sub>2</sub>TiO<sub>4</sub> crystallises in the monoclinic P2<sub>1</sub>/n β-phase shown in figure 1a (alternative view provided in figure ??). This structure has 4 distinct O<sup>2-</sup> sites, 2 Ba<sup>2+</sup> sites and 1 Ti<sup>4+</sup> site. The Ba<sub>I</sub> and Ba<sub>II</sub> sites are coordinated to 7 and 8 O<sup>2-</sup> ions respectively, while each Ti ion is coordinated tetrahedrally to 4 O<sup>2-</sup> ions.<sup>15,44</sup> These isolated tetrahedra alternate with Ba<sub>I</sub> ions to form TiO<sub>4</sub>-Ba<sub>I</sub> channels down the *b*-axis. The high tem-

Table 2 Comparison of calculated and experimental lattice parameters of the (a) β and (b) α' phases of Ba<sub>2</sub>TiO<sub>4</sub>.

(a) Lattice parameters of β-Ba <sub>2</sub> TiO <sub>4</sub>			
Parameter	Experimental <sup>15</sup>	Calculated	Difference (%)
a (Å)	6.096(4)	6.100	0.004 ( 0.06)
b (Å)	7.681(6)	7.676	-0.005 (-0.07)
c (Å)	10.545(9)	10.488	-0.057 (-0.54)
α=γ (°)	90.000	90.000	0.000 ( 0.00)
β (°)	92.990(6)	93.425	0.435 ( 0.47)
(b) Lattice parameters of α'-Ba <sub>2</sub> TiO <sub>4</sub>			
Parameter	Experimental <sup>16</sup>	Calculated	Difference (%)
a (Å)	6.107(8)	6.118	0.011 ( 0.18)
b (Å)	22.952(4)	22.969	0.017 ( 0.08)
c (Å)	10.540(2)	10.476	-0.064 (-0.61)
α=β=γ(°)	90.000	90.000	0.000 ( 0.00)

Experimental standard deviations of the last digit given in the parenthesis of the first column.

perature orthorhombic P2<sub>1</sub>nb α'-phase, shown in figure 1b, is a tripled *b*-axis superstructure of the β-phase, and therefore shares the same basic structure. The α'-phase contains 6 symmetrically inequivalent Ba sites, however, sites Ba<sub>I</sub>-Ba<sub>III</sub> are similar to an under-coordinated β-Ba<sub>I</sub> site and sites Ba<sub>IV</sub>-Ba<sub>VI</sub> are comparable to β-Ba<sub>II</sub>. Likewise, the 3 unique tetrahedra in the α'-phase are similar to those of the β-phase but with slightly different orientations.

Using the inter-ionic potentials listed in Table1, the calculated lattice parameters of both β and α'-phase Ba<sub>2</sub>TiO<sub>4</sub> shows good fit to within 1% of the experimental crystal structure, table 2.<sup>15,16</sup> The cation-anion distances, given for the β-phase in table ??, are also found to be in reasonable agreement, despite the ambiguous experimental crystal structure. The search for transferable inter-ionic potential models is not trivial particularly when the differences between the phases are so subtle.

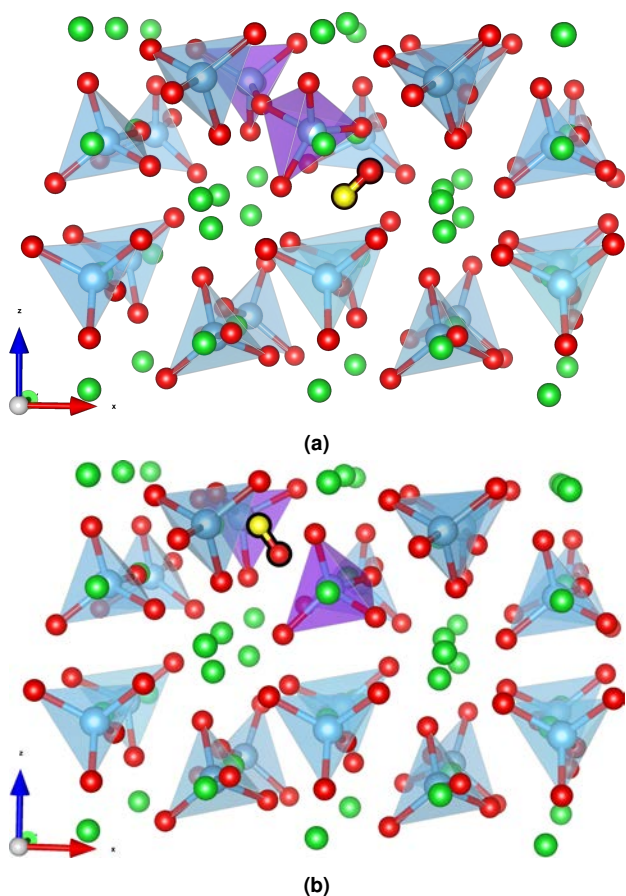
The calculated point defect energies, presented in table ??, suggest the formation of intrinsic defects in both phases of Ba<sub>2</sub>TiO<sub>4</sub> to be energetically unfavourable. Therefore, the concentration of such defects, even at high temperatures, will be negligible and undoped Ba<sub>2</sub>TiO<sub>4</sub> is likely to be a poor oxide ion conductor. This is not unexpected given that similar findings have been reported for the isostructural material β-Ca<sub>2</sub>SiO<sub>4</sub>.<sup>44</sup>

3.2 Water Incorporation

Ba<sub>2</sub>TiO<sub>4</sub> is a hygroscopic material and particularly at elevated temperatures, tends to decompose on contact with humid air.<sup>45,46</sup> However, it may be feasible for small concentrations of water to be incorporated into Ba<sub>2</sub>TiO<sub>4</sub> as protonic defects with minimal decomposition. In some materials, the defects formed upon water incorporation lead to enhanced proton and oxide ion conductivities.<sup>34,47</sup> For these reasons, the favourability of protonic defects have been investigated.

In the first stage, the proton defect location and energy were determined. Our simulations suggest protonic defects will bind to oxide ions and therefore have been treated as hydroxide units





**Fig. 2** a)  $\text{HO}_\text{O}^\bullet$  and b)  $\text{OH}_\text{i}^\bullet$  defect in  $\alpha'$ - $\text{Ba}_2\text{TiO}_4$  with Ba, Ti, O and H ions shown as green, blue, red and yellow spheres respectively and  $\text{TiO}_4$  tetrahedra in blue, purple polyhedra represent “ $\text{Ti}_2\text{O}_7$ ” units in sub-figure a and distorted- $\text{TiO}_4$  units in sub-figure b.

( $\text{OH}^-$ ). Equations 5 to 8 represent the viable mechanisms by which water can be incorporated either on lattice oxide sites ( $\text{OH}_\text{O}^\bullet$ ) or interstitial sites ( $\text{OH}_\text{i}^\bullet$ ).<sup>48</sup> A series of Mott-Littleton calculations were carried out to determine the energies, structures and locations of these defects.

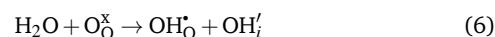
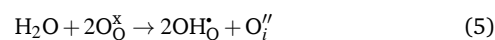
In the lowest energy  $\alpha'$ -phase structure, figure 2a, the hydroxide's oxygen remains at the original  $\text{O}_\text{III}$  lattice site, and a single oxygen bridged “ $\text{Ti}_2\text{O}_7$ ” unit is formed reminiscent of the “ $\text{Ga}_2\text{O}_7$ ” units seen in the structurally related  $\text{La}_{0.8}\text{Ba}_{1.2}\text{GaO}_{3.9}$ .<sup>49</sup> With a shortest HO-Ti distance of  $\sim 2.4$  Å the  $\text{OH}^-$  lies primarily on the outside of the Ti ion's coordination sphere. The  $\text{OH}_\text{i}^\bullet$  defect structure, figure 2b, shows that the hydroxide's oxygen lies approximately halfway between a pair of nearest neighbouring Ti ions. Although the hydroxide unit is  $\sim 2.5$  Å away from the two Ti ions its presence does distort the neighbouring  $\text{O}_\text{I}$  sites, albeit to a lesser extent than that seen for the  $\text{OH}_\text{O}^\bullet$  defect.

Following the determination of the most favourable location for the proton defects, the various mechanisms of water incorporation were considered in order to determine the water incorporation energies. The first two mechanisms, represent water incorporated as  $\text{OH}_\text{O}^\bullet$  units and an oxygen or hydroxyl interstitial, shown in equations 5 and 6. This is achieved through the forma-

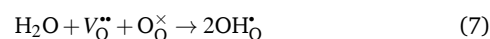
**Table 3** Water incorporation energies (eV) for mechanisms 5 to 8.

Equation	$\beta$ -phase	$\alpha'$ -phase
5: $\text{H}_2\text{O} = 2\text{OH}_\text{O}^\bullet + \text{O}_\text{i}'' + \text{E}_\text{PT}$	7.80	7.17
6: $\text{H}_2\text{O} = \text{OH}_\text{O}^\bullet + \text{OH}_\text{i}^\bullet + \text{E}_\text{PT}$	4.32	3.96
7: $\text{H}_2\text{O} = 2\text{OH}_\text{O}^\bullet - \text{V}_\text{O}^\bullet + \text{E}_\text{PT}$	0.83	0.47
8: $\text{H}_2\text{O} = 2\text{OH}_\text{i}^\bullet - \text{O}_\text{i}'' + \text{E}_\text{PT}$	0.85	0.75

tion of combinations of  $\text{OH}_\text{O}^\bullet$  defects and  $\text{OH}_\text{i}^\bullet$  defects. The first mechanism has been proposed to increase oxide ion conductivity in some materials due to the oxygen interstitials it formation.<sup>34</sup>



The mechanisms considered in equations 7 and 8 are specific to the presence of oxygen vacancies or interstitials in  $\text{Ba}_2\text{TiO}_4$ . In equation 7,  $\text{H}_2\text{O}$  reacts with an oxygen vacancy to form a pair of  $\text{OH}_\text{O}^\bullet$  units. This mechanism is responsible for proton conduction in some  $\text{A}_2\text{BO}_4$ -type materials.<sup>47,50,51</sup> In equation 8,  $\text{H}_2\text{O}$  reacts with an oxygen interstitial forming a pair of  $\text{OH}_\text{i}^\bullet$  defects. If favourable, these two mechanisms would eliminate any oxygen defects present, such as those formed through doping, (see supplementary material for further information) and are therefore likely to curb oxide ion conduction.



Water incorporation energies ( $\text{E}_\text{H}_2\text{O}$ ) for these mechanisms are presented in table 3 and were calculated using the equations listed therein. In this study, an  $\text{E}_\text{PT}$  value of -9.74 eV was selected, which represents the energy of the gas phase proton transfer reaction  $\text{H}_2\text{O} + \text{O}^{2-} \rightarrow 2\text{OH}^-$ .<sup>52</sup> Our calculations suggest that water incorporation via mechanisms 5 and 6 is unfavourable, indicating that significant water inclusions are unlikely in pristine  $\text{Ba}_2\text{TiO}_4$ . However, water incorporation via the oxide defect interaction mechanisms 7 and 8 are more favourable with much lower incorporation energies.. This suggests that oxide ion defects formed in  $\text{Ba}_2\text{TiO}_4$  as a result of doping may be supplanted by hydroxide ions and possibly reducing oxide ion conductivities, see supplementary information for some examples of water incorporation on doping. Furthermore, as their incorporation into the  $\alpha'$ -phase is more favourable water based defects, if present, may stabilise the  $\alpha'$ -phase at lower temperatures in a similar fashion to doping.<sup>17,18</sup>

### 3.3 Carbon Dioxide Incorporation (Modelling Studies)

As  $\text{Ba}_2\text{TiO}_4$  is commonly synthesised via the carbonate route, small concentrations of  $\text{CO}_2$  based impurity defects are likely, particularly at low synthesis temperatures. Furthermore, there is growing evidence of  $\text{CO}_2$  incorporation as a carbonate ion in many systems prepared by lower temperature routes, e.g. reports of carbonate incorporation in perovskites, Hancock *et al.*<sup>21</sup>,

**Table 4** Carbon dioxide incorporation energies for mechanisms 9 to 13.

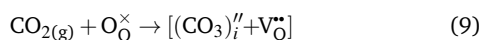
Equation	Defect Energy (eV)	
	$\beta$ -phase	$\alpha'$ -phase
9: $E_{\text{CO}_2} = [(\text{CO}_3)_i'' + \text{V}_\text{O}^{\bullet\bullet}] + E_{\text{OT}}$	0.35	-0.05
10: $E_{\text{CO}_2} = (\text{CO}_3)_i'' + \text{V}_\text{O}^{\bullet\bullet} + E_{\text{OT}}$	4.99	4.23
11: $E_{\text{CO}_2} = (\text{CO}_3)_i'' - \text{O}_i'' + E_{\text{OT}}$	-1.97	-2.47
12: $E_{\text{CO}_2} = [(\text{CO}_3)_i'' + 2\text{V}_\text{O}^{\bullet\bullet}] + E_{\text{OT}} - \text{V}_\text{O}^{\bullet\bullet}$	-3.08	-3.24
13: $E_{\text{CO}_2} = \frac{1}{2}[(\text{CO}_3)_i'' + 2\text{V}_\text{O}^{\bullet\bullet}] + E_{\text{OT}} + \frac{1}{2}(\text{CO}_3)_i''$	0.96	0.49

and the recent report showing that “YAlO<sub>3</sub>” is actually an oxide carbonate, of form Y<sub>3</sub>Al<sub>3</sub>O<sub>8</sub>CO<sub>3</sub>.<sup>53</sup> among others.<sup>43,53,54</sup> Indeed below 750 °C Ba<sub>2</sub>TiO<sub>4</sub> is known to react with CO<sub>2</sub> to form BaCO<sub>3</sub> and BaTiO<sub>3</sub>, however, this reaction reverses at higher temperatures.<sup>18</sup> While Ba<sub>2</sub>TiO<sub>4</sub> has been studied for its CO<sub>2</sub> sorption properties, investigations focused on macroscopic rather than atomistic effects.<sup>9,10,18,20,55</sup>

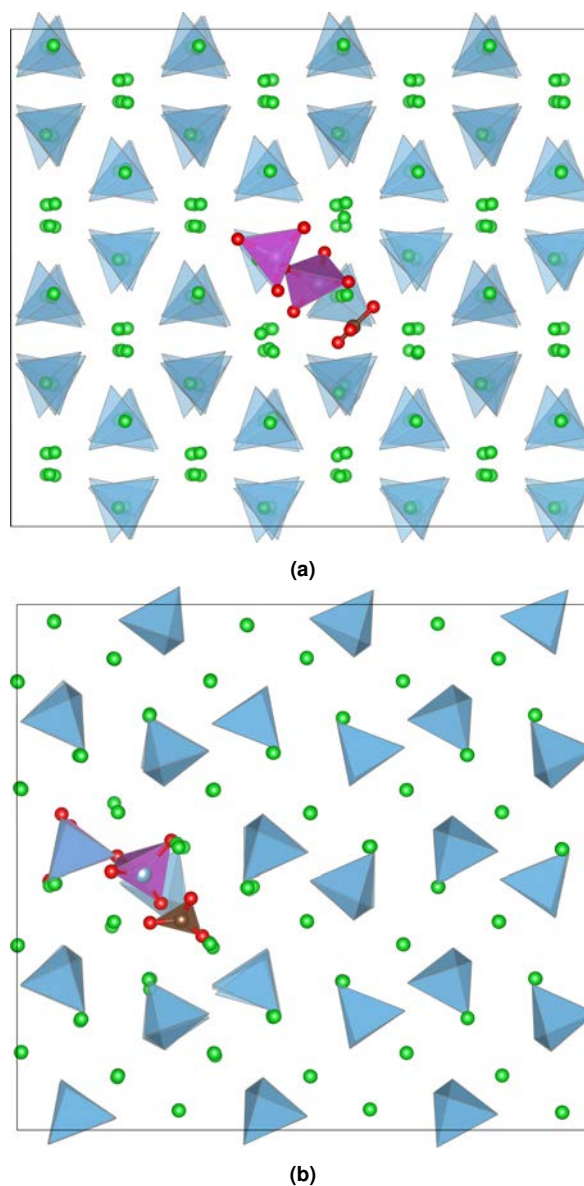
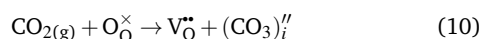
During Ba<sub>2</sub>TiO<sub>4</sub> decomposition, it has been proposed that CO<sub>2</sub> reacts at the surface, where there will be more defects, to form CO<sub>3</sub><sup>2-</sup> and finally BaCO<sub>3</sub>.<sup>20</sup> Particularly during synthesis, CO<sub>2</sub> may react with an interstitial or lattice oxide ion to produce a carbonate anion. Therefore, CO<sub>2</sub> based defects were treated as CO<sub>3</sub><sup>2-</sup> ions in this investigation to determine whether bulk carbonate defects may form favourably through combination of CO<sub>2</sub> and lattice oxygen.

To correctly calculate the CO<sub>2</sub> incorporation energies ( $E_{\text{CO}_2}$ ) a term, similar to the proton transfer term ( $E_{\text{PT}}$ ), must be included to represent the energy of the reaction  $\text{CO}_2 + \text{O}^{2-} \rightarrow \text{CO}_3^{2-}$ . As no value for this term (referred to as  $E_{\text{OT}}$ ) exists in literature a value of -14.37 eV has been derived in this work following the procedure detailed in the supplementary material. All carbonate defect calculations were conducted in  $\beta$ -4 × 3 × 2 and  $\alpha'$ -4 × 1 × 2 supercells.

Five CO<sub>2</sub> incorporation mechanisms were considered (equation 9 - 13). In equation 9, CO<sub>2</sub> reacts with a lattice oxide ion to form a carbonate interstitial with an oxygen vacancy  $[(\text{CO}_3)_i'' + \text{V}_\text{O}^{\bullet\bullet}]$  at the nearest neighbour tetrahedra. It should be noted that square brackets denote clustered defects, and so requires an additional binding energy term (-4.28 eV) calculated as the difference between a carbonate group next to an oxygen vacancy and a carbonate group infinitely separated from the oxygen vacancy.

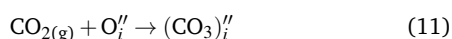


It can be seen from the calculated  $E_{\text{CO}_2}$  values in table 4 that this mechanism is favourable, particularly in the  $\alpha'$ -phase, suggesting that such defects are likely in pristine Ba<sub>2</sub>TiO<sub>4</sub> in accord with the experimental data. All subsequent discussions regarding carbonate defect structures will focus on those in the  $\alpha'$ -phase as they are the most favourable, see table 4. Rather than forming a joint tetrahedra-carbonate defect like those seen in Y<sub>3</sub>Al<sub>3</sub>O<sub>8</sub>CO<sub>3</sub>, the CO<sub>3</sub><sup>2-</sup> groups prefer to remain independent<sup>53</sup> but clustered with the “Ti<sub>2</sub>O<sub>7</sub>” units which form as a result of oxygen vacancy, figure 3.

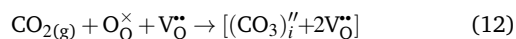


**Fig. 3**  $[(\text{CO}_3)_i'' + \text{V}_\text{O}^{\bullet\bullet}]$  defect in  $\alpha'$ -Ba<sub>2</sub>TiO<sub>4</sub>. Green, blue, red and brown spheres indicate Ba, Ti, O and C ions respectively, and blue, purple and brown polyhedra TiO<sub>4</sub>, “Ti<sub>2</sub>O<sub>7</sub>” and CO<sub>3</sub><sup>2-</sup> units. As viewed on the *ac* (a) and *bc*-planes (b).

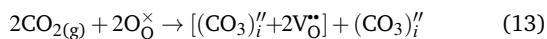
The second mechanism, shown in equation 10, is comparable to the previous but with its  $(\text{CO}_3)_i''$  and  $\text{V}_\text{O}^\bullet$  unclustered. The comparably high energy of this mechanism, table 4, shows a significant clustering force exists between the  $\text{V}_\text{O}^\bullet$  and  $(\text{CO}_3)_i''$ , suggesting that oxygen vacancies will be trapped and immobile. Having established the favourability of  $\text{CO}_2$  incorporation in pristine  $\text{Ba}_2\text{TiO}_4$ , attention is turned to the possible interactions with other defects e.g. oxygen interstitials or vacancies which might be induced through doping.



Carbonates defects could be formed through the reaction of  $\text{CO}_2$  with an oxygen interstitial, as shown in equation 11. With an  $E_{\text{CO}_2}$  value of -2.47 eV this mechanism is highly favourable and suggests that any oxygen interstitials present could be readily annihilated. Again, the carbonate defect is noticeably more stable in the high temperature phase. The  $(\text{CO}_3)_i''$  defect structure is shown in figure 4, which shows that the carbonate group is accommodated by a displacement of the neighbouring  $\text{TiO}_4$  tetrahedra. It is interesting to note that the local arrangement of the Ba ions around the  $(\text{CO}_3)_i''$  conforms to that seen in  $\text{BaCO}_3$ , which is one of the by-products of the  $\text{Ba}_2\text{TiO}_4$ - $\text{CO}_2$  reaction.

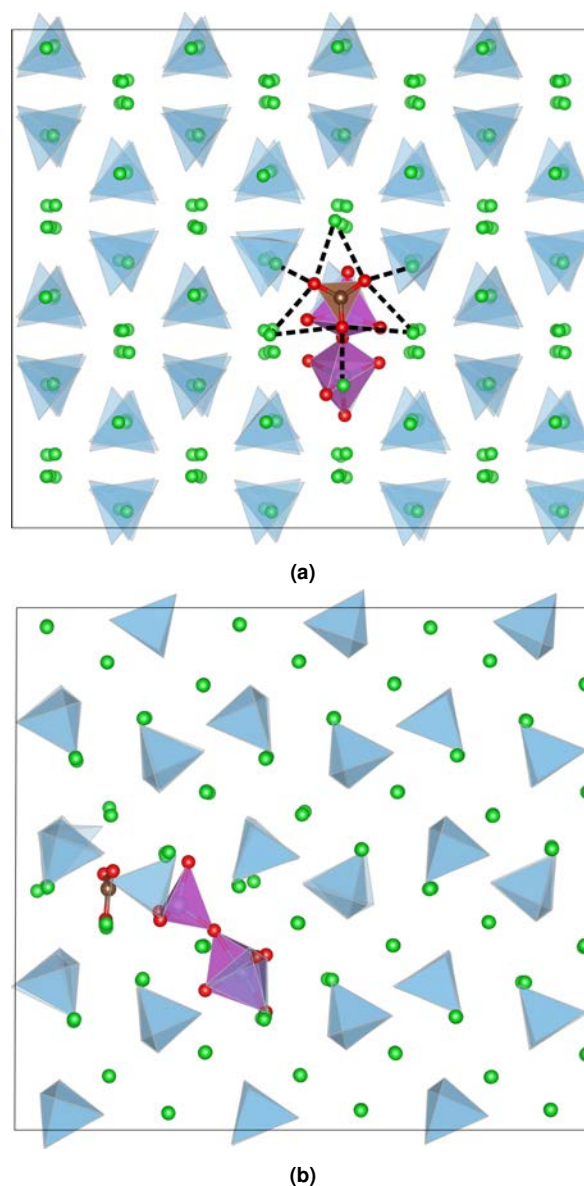


Interactions between oxygen vacancies and carbonate defects were also considered. However, such interactions will be associative rather than a direct reaction. Mechanism 12 represents formation and further clustering of a  $[(\text{CO}_3)_i'' + \text{V}_\text{O}^\bullet]$  defect to an oxygen vacancy. This is analogous to mechanism 9 with a second oxygen vacancy clustering augment. It can be seen from the energy of this mechanism, -3.24 eV, that the presence of oxygen vacancies will dramatically increase the favourability of carbon dioxide incorporation. Taking the difference of mechanism 9 and 12 gives a clustering energy of -3.19 eV suggesting oxygen vacancies formed through doping would be strongly bound to carbonate impurity defects. It can be seen from figure 5 that the presence of such a defect causes significant structural distortions in the  $\text{Ba}_2\text{TiO}_4$  lattice and results in the formation of a " $\text{Ti}_3\text{O}_{10}$ " units in which the central Ti ion has 4 bridging oxygens.



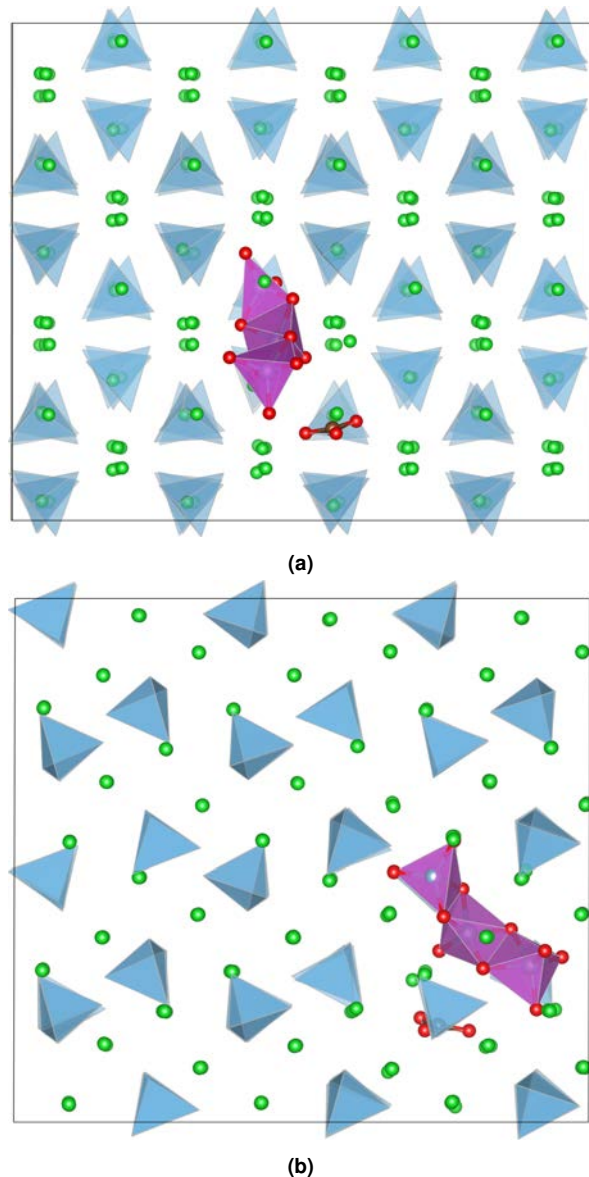
The final mechanism, considered in equation 13, is found to offer another low energy route towards  $\text{CO}_2$  incorporation in pristine  $\text{Ba}_2\text{TiO}_4$ . This mechanism can be thought of as the combination of mechanisms 11 and 12 with an oxygen Frenkel defect.

Finally, because carbonate defects are more stable in the  $\alpha'$ -phase than the  $\beta$ -phase, the  $\alpha'$ -phase may be stabilised by the presence of small concentrations of carbonate impurities. In this respect there have been reports that the high temperature  $\alpha'$ -phase can be observed in lower temperature synthesis routes, which has been attributed to particle size effects, but may be due instead to small concentrations of carbonate impurities.<sup>17-20</sup> Notably the modelling results showed favourable  $\text{CO}_2$  incorporation in  $\alpha'$ - $\text{Ba}_2\text{TiO}_4$  in the absence of defects, while the presence of ox-

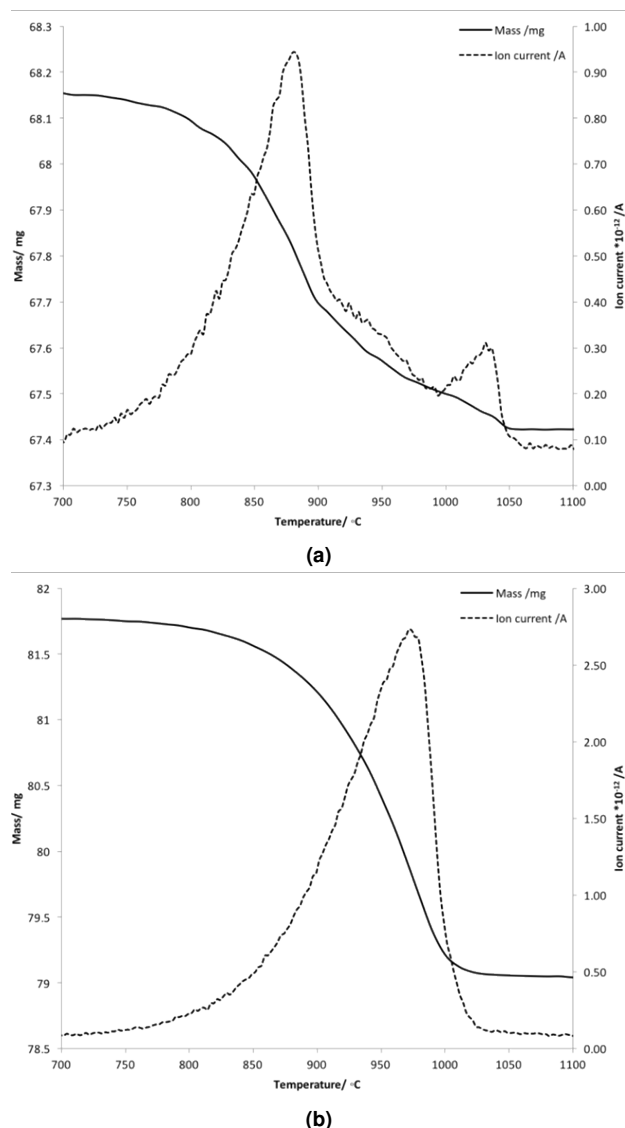


**Fig. 4**  $(\text{CO}_3)_i''$  defect in  $\alpha'$ - $\text{Ba}_2\text{TiO}_4$ , image key identical to figure 3 but with purple polyhedra indicating a " $\text{Ti}_2\text{O}_8$ " unit. Dashed lines illustrate the  $\text{CO}_3^{2-}$ -Ba arrangements in common with  $\text{BaCO}_3$ . As viewed on the *ac* (a) and *bc*-planes (b).





**Fig. 5**  $[(\text{CO}_3)']_f + 2V_{\text{O}}^{\bullet\bullet}$  defect in  $\alpha'$ - $\text{Ba}_2\text{TiO}_4$ , image key identical to figure 3 but with purple polyhedra indicating oxygen deficient " $\text{Ti}_3\text{O}_{10}$ ". As viewed on the  $ac$  (a) and  $bc$ -planes (b).



**Fig. 6** (a) TG trace for orthorhombic  $\text{Ba}_2\text{TiO}_4$  (prepared by annealing monoclinic  $\text{Ba}_2\text{TiO}_4$  at  $450^\circ\text{C}$  for 8 hours in air, with an intermediate regrind). The MS trace (dashed line) shows mass losses due to  $\text{CO}_2$ . The first mass loss is attributed to  $\text{CO}_2$  mass loss from orthorhombic  $\text{Ba}_2\text{TiO}_4$  indicating a composition for this phase of  $\text{Ba}_2\text{TiO}_{4-0.09}\text{CO}_2$  (or  $\text{Ba}_2\text{TiO}_{3.91}(\text{CO}_3)_{0.09}$  to emphasise the incorporation as carbonate). The higher temperature mass loss is attributed to the partial decomposition of some  $\text{Ba}_2\text{TiO}_4$  to give  $\text{BaCO}_3$  and  $\text{BaTiO}_3$  which recombines to form  $\text{Ba}_2\text{TiO}_4$  at elevated temperatures. This assignment is supported by TGA studies of a sample of  $\text{Ba}_2\text{TiO}_4$  (b) which has been slow cooled ( $30^\circ\text{C}/\text{hour}$ ) in air to room temperature, for which much higher  $\text{BaCO}_3$  levels were observed. In this case a much greater mass loss is observed, with the TGA trace dominated by the mass loss in the higher temperature region.

ide ion vacancy or interstitial defects made the process even more favourable. Thus at the surface where defects would be more abundant due to the broken symmetry of the crystal, this CO<sub>2</sub> incorporation process is likely to be highly favourable. Furthermore, a few examples of solution energies when taking doping into considerations have been shown in the supplementary, but since there is a fuller paper on the effects of doping in manuscript, further details on this will follow.

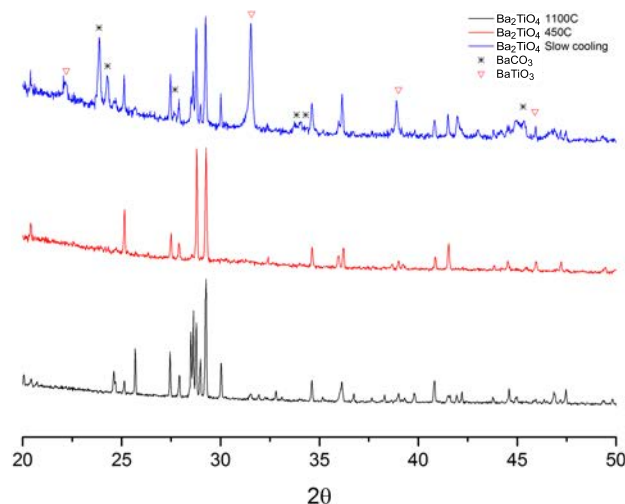
### 3.4 Carbon Dioxide Incorporation (Experimental Studies)

Following on from prior literature reports that  $\alpha'$ -Ba<sub>2</sub>TiO<sub>4</sub> was obtained by synthesis at lower temperatures and the modelling predictions that CO<sub>2</sub> incorporation was favourable in this phase, even in the absence of defects, experimental studies were performed to confirm the presence of carbonate. In this work, samples of monoclinic  $\beta$ -Ba<sub>2</sub>TiO<sub>4</sub> were prepared and heat treated under different conditions. The results showed that slow cooling (0.5 °C min<sup>-1</sup>) from 950 °C in N<sub>2</sub> led to no change in X-ray diffraction pattern, while a similar heat treatment in air led to a partial change from monoclinic to orthorhombic Ba<sub>2</sub>TiO<sub>4</sub>. However, in addition to the presence of both  $\alpha'$  and  $\beta$ -phases, such a heat treatment also gave large BaCO<sub>3</sub> and BaTiO<sub>3</sub> impurities and so further experiments were performed heating in air for 6-8 hours at temperatures < 900 °C in order to optimise the conditions for the formation of orthorhombic Ba<sub>2</sub>TiO<sub>4</sub>, while limiting the partial decomposition to BaCO<sub>3</sub> and BaTiO<sub>3</sub>. These experiments showed temperatures < 750 °C led to the appearance of the orthorhombic Ba<sub>2</sub>TiO<sub>4</sub> phase, with the optimum temperature being 450 °C (figure 7). TG-MS analysis of this phase under N<sub>2</sub> showed a small mass loss at 880 °C, which MS data showed was due to CO<sub>2</sub> loss. A composition of Ba<sub>2</sub>TiO<sub>4</sub>·0.09CO<sub>2</sub> (or Ba<sub>2</sub>TiO<sub>3.91</sub>(CO<sub>3</sub>)<sub>0.09</sub> to emphasise the incorporation as carbonate) was indicated, figure 6. After the TG-MS experiment the phase obtained was monoclinic  $\beta$ -Ba<sub>2</sub>TiO<sub>4</sub>. Therefore these results strongly align with the modelling studies supporting the conclusion that the alpha phase is stabilised by low levels of carbonate defects, which would explain prior reports of its formation by low temperature routes<sup>17-20</sup>, since at the temperatures employed residual carbonate is likely to be present. Furthermore it indicates that the reaction of Ba<sub>2</sub>TiO<sub>4</sub> with CO<sub>2</sub> is not just limited to the surface, but rather is a mixture of bulk (migration of CO<sub>2</sub>, as CO<sub>3</sub><sup>2-</sup>, into the bulk phase) and surface processes.

## 4 Conclusions

In conclusion, this detailed computational study backed up by experimental results show:

- 1) that intrinsic defects will not form naturally in any significant quantity in Ba<sub>2</sub>TiO<sub>4</sub>
- 2) CO<sub>3</sub><sup>2-</sup> defects are likely to be common impurities in both pristine and doped Ba<sub>2</sub>TiO<sub>4</sub> systems; whereas those based on H<sub>2</sub>O are predicted only to form in systems which contain other supporting defects, such as oxygen vacancies or interstitials. Both carbonate and protonic defects are predicted to trap oxide ion defects.
- 3) that the  $\alpha'$ -phase stabilising abilities of carbonate and protonic defects may, in part, account for the varied reports of Ba<sub>2</sub>TiO<sub>4</sub>'s



**Fig. 7** XRD patterns for Ba<sub>2</sub>TiO<sub>4</sub> heated under different conditions. Black: as prepared at 1100 °C in air and furnace cooled, showing the presence of monoclinic Ba<sub>2</sub>TiO<sub>4</sub>. Red: sample annealed at 450 °C in air for 8 hours with an intermediate regrind, showing the presence of orthorhombic “Ba<sub>2</sub>TiO<sub>4</sub>”: TGA studies (figure 6) suggest a composition for this phase of Ba<sub>2</sub>TiO<sub>4</sub>·0.09CO<sub>2</sub> (or Ba<sub>2</sub>TiO<sub>3.91</sub>(CO<sub>3</sub>)<sub>0.09</sub> to emphasise the incorporation as carbonate). Blue: sample slow cooled in air at 30 °C/hour, showing significant decomposition to BaCO<sub>3</sub> and BaTiO<sub>3</sub>.

phase behaviour, with our own experimental studies showing that this phase can be formed from the  $\beta$ -phase by heating in air at 450 °C for 6 hours, with TG studies confirming the presence of carbonate in the sample.

The work therefore highlights the importance of the consideration of the possible effect of CO<sub>2</sub> (incorporated as CO<sub>3</sub><sup>2-</sup>) to rationalise the structure and properties of mixed metal oxide systems. Such consideration is also especially important, when one considers the growing use of lower temperature sol gel routes for the design and synthesis of new functional materials. Such routes are typically C rich, and so may introduce significant residual carbonate into the material, and so there is therefore a clear need to investigate the carbonate content of low temperature (<1000 °C) synthesised materials, and examine how this may affect the structure and properties.

While these studies have shown some interesting results, they only relate to the materials bulk. However, it is possible that surface defect phenomena may also play an important role. Thus, further work must be conducted to investigate defect behaviour at the surface of Ba<sub>2</sub>TiO<sub>4</sub>.

## 5 Acknowledgments

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## 6 Supporting Information

An appendix document accompanying this work contains additional supporting information in the form of: Interatomic potentials for  $\text{OH}^-$  and  $\text{CO}_3^{2-}$ ; The derivation of carbonate's oxygen transfer term ( $E_{OT}$ ); Intrinsic defect energies; An  $a$ -axial view of  $\beta\text{-Ba}_2\text{TiO}_4$ ; Water and carbon dioxide incorporation mechanisms involving dopants to facilitate oxide ion defect formation; A table comparing interatomic distances; and another containing isolated point defect energies.

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